

General Structure of the Thomas-Fermi Equation of State

George A. Baker, Jr. and J. D. Johnson

Theoretical Division, Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545

By perturbation methods we derive the behavior of the Thomas-Fermi equation of state near both the “hot-curve” and the “cold-curve.” By Padé methods we derive efficient computational formulae for the coefficients in these expansions. We are able to meld all these results into a structurally correct representation of the Thomas-Fermi fluid pressure. We indicate how this representational structure can be used to construct the equation of state for realistic materials over large ranges of temperature and pressure. We also discuss the computation of the degree of ionization with and without the exchange correction.

Suggested PACS index numbers: 5.70.Ce, 5.30.Fk, 64.10.+h, 67.20.+k

I. INTRODUCTION AND SUMMARY

The statistical theory of the atom due to Thomas and Fermi,¹ with modifications due to Dirac² has been used for a long time as a basis for computing the equation of state of electron-ion fluids.³ Although it has been recognized for some time that this model has a number of quantitative inaccuracies, *e.g.*, that its zero temperature behavior is in bad agreement with the experimental binding energies,⁴ it has also been the case that a lot of correct physics is built into the model and we think that the study of this structure may well be enlightening in order to construct better equations of state. In a previous paper⁵ we began this study. We showed that in the “high-temperature limit” that the Thomas-Fermi model reduced (correctly) to the ideal Fermi gas. That is to say that when the Debye screening length, which is proportional to e^2/kT is small compared to the interparticle spacing, that for any de Broglie length, (proportional to h/\sqrt{mkT}) the Thomas-Fermi model reduces to the corresponding ideal Fermi gas limit. (Here and throughout we denote the electronic charge by e , Boltzmann’s constant by k , the absolute temperature by T , Planck’s constant by h and the electron mass by m . This result completed the necessary investigations of the various limiting regions of the equation of state, because it was already known that:

(i) In the low density limit at fixed temperature, both the Debye and the de Broglie lengths go to zero. (Here and subsequently in this catalogue of cases when we refer to the Debye and de Broglie lengths we will mean in units of the interparticle spacing.) Also the atoms become completely ionized and the “electronic contribution,” for example to the pressure, becomes the ideal gas law,

$$P\Omega = ZNkT, \quad (1.1)$$

where we denote, here and throughout, the pressure by P , the volume by Ω , the number of atoms by N and the nuclear charge which is also taken as the number of electrons per atom by Z . This case agrees precisely with

the zero de Broglie length limit of the hot curve. By the hot curve we mean the limit as $T \rightarrow \infty$ for fixed de Broglie length.

(ii) For the zero temperature limit at fixed density (both the Debye and the deBroglie lengths tend to infinity), the “electronic contribution” to (again for example) the pressure, becomes the cold curve,³

$$P\Omega/N = Z^{\frac{2}{3}}\phi(Z\Omega/N), \quad (1.2)$$

where $\phi(x)$ is a well defined function. By the cold curve we mean the zero temperature isotherm.

(iii) In the limit as the de Broglie length goes to infinity, the pressure becomes independent of the temperature. This result is explicitly the case for the hot curve and gives the degenerate electron gas pressure. In this limit the kinetic energy scales as the density to the five-thirds power and so dominates the potential energy which only increases like the density to the four-thirds power. Thus the limit becomes independent of the Debye length. This situation is illustrated by the fact that for $T = 0$ [case (ii) above] we get the same high-density limit as we do for the hot curve.

(iv) There only remains to consider the case where the temperature goes to zero when the density goes to zero. Here we have a complicated region that unfortunately is physically not well illuminated by the Thomas-Fermi model as the behavior here depends on phase transitions, ionization potentials, *etc.* We do not expect the present study to adequately represent the physics of this region.

We have spoken of electronic contributions as though they were separable from the ionic contributions as independent contributions to the pressure, which of course they can not be, any more than we can physically separate the radiation pressure from the rest of the system. We make this artificial separation as a matter of convention. For the purpose of this paper, we presume a treatment of the ionic contributions which merely assumes that they obey Maxwell-Boltzmann statistics and add an ideal gas contribution to the pressure for them. In the

spirit of the Thomas-Fermi approach, we think of Z electrons encased in an impermeable sphere around a fixed nuclear center, exerting the pressure on the surrounding spherical shell. The purpose of the study is to gain insight into the structure of the Thomas-Fermi equation of state, rather than to pretend that all aspects are physically realistic.

The principal result that we obtain is a representational structure which embodies the correct behavior on and near both the “hot-curve” and the “cold-curve,” as well as smoothly interpolating in a structurally correct manner between them. This general representational structure appears to us to be adaptable in a straightforward manner to real substances.

In the second section, we compute by perturbation methods the leading corrections in powers of the ratio of the Debye length to the interparticle spacing for the ideal-Fermi-gas electron-pressure in the Thomas-Fermi model. In the third section we show how the coefficients of this expansion can be re-expressed in terms of the ratio of the de Broglie length to the interparticle spacing, and how they also lead to the coefficients in the expansions of the Helmholtz free energy and the internal energy. In the fourth section, we show how these coefficients can be efficiently computed by direct Padé approximant methods. In addition we show how to compute the degree of ionization (no exchange correction case) from the pressure. In the fifth section, we provide a description, adequate for our purposes, of the Thomas-Fermi cold-curve and the leading correction in temperature to it. In the sixth section we develop our global representation of the pressure for the Thomas-Fermi model and discuss its comparison with direct numerical computation of the model pressure. In the final section we discuss the way in which this representation can be used to generate equations of state for realistic substances. We also evaluate the exact exchange correction and discuss the computation of the degree of ionization with the exchange correction included.

II. PERTURBATIONS OFF THE HOT CURVE OF THE SOLUTION OF THE THOMAS-FERMI INTEGRO-DIFFERENTIAL EQUATION

In a previous paper⁵ we showed that the limit of the Thomas-Fermi theory of the thermodynamic behavior of gases when the Debye screening length is negligible compared to the interparticle distance is just the ideal Fermi gas. In this section we compute the leading perturbation corrections to this limit in terms of a small, but non-zero Debye length. As a reminder of the basics of Thomas-Fermi theory, we give the expression for the density,

$$\rho = \int_0^\infty \frac{2 \cdot 4\pi p^2 dp / h^3}{\exp[(p^2/2m - eV)/kT + \eta]}, \quad (2.1)$$

where $-eV$ is the potential energy. It is convenient to

define the auxiliary functions

$$I_n(\eta) = \int_0^\infty \frac{y^n dy}{\exp(y - \eta) + 1}. \quad (2.2)$$

The Poisson equation is then used to determine $V(r)$. It yields

$$\frac{1}{r} \frac{d^2}{dr^2}(rV(r)) = \frac{16\pi^2}{h^3} e(2mkT)^{\frac{3}{2}} I_{\frac{1}{2}} \left(\frac{eV(r)}{kT} - \eta \right). \quad (2.3)$$

The boundary conditions for this equation are that

$$\lim_{r \rightarrow 0} rV(r) = Ze, \quad (2.4)$$

where Z is the nuclear charge, and the integral of $\rho(r)$ over a sphere of radius r_b is equal to Z for electrical neutrality. If Ω is the volume and N is the number of atoms, then

$$\Omega = \frac{4\pi}{3} r_b^3 N, \quad (2.5)$$

defines the “spherical atom” approximation which is used. The idea is that regularly spaced atoms can be enclosed, each in its own individual region of space which is not so different from a sphere, and that these isolated atoms interact with their neighbors only through their surface electron behavior.

It is convenient to our purposes to define the constants,

$$c = \left(\frac{h^3}{32\pi^2 e^2 m (2mkT)^{\frac{1}{2}}} \right)^{\frac{1}{2}} \propto T^{-\frac{1}{4}}, \quad (2.6)$$

and

$$\alpha = Ze^2/kTc \propto T^{-\frac{3}{4}}. \quad (2.7)$$

Now, following Baker and Johnson,⁵ we make the change of variables to the appropriate high-temperature ones,

$$\sigma = \frac{r}{c\alpha^{1/3}}, \quad \gamma(\sigma)/\sigma = (eV(r)/kT) - \eta. \quad (2.8)$$

The equations and boundary conditions now become,

$$\frac{d^2\gamma}{d\sigma^2} = \alpha^{\frac{2}{3}} \sigma I_{\frac{1}{2}} \left(\frac{\gamma}{\sigma} \right), \quad (2.9)$$

$$\gamma(0) = \alpha^{\frac{2}{3}}, \text{ and} \quad (2.10)$$

$$\frac{d\gamma}{d\sigma} = \frac{\gamma}{\sigma}, \text{ at the boundary.} \quad (2.11)$$

For ease of exposition, we will derive the leading order correction first. It is of the order of an exchange correction, but as Thomas-Fermi theory does not have the exchange energy in it, we identify this correction as the Thomas-Fermi theory version of the Debye-Huckel correction. After this term is calculated we will go on to compute the next order perturbation term off the hot curve, which is of the order of the standard Debye-Huckel correction. It turns out to vanish. We finish up this

section by computing one additional order in the perturbation expansion. A handy identity which we will use is,

$$I'_n(\eta) = nI_{n-1}(\eta), \quad n > 0, \quad (2.12)$$

for the functions defined in (2.2). The solution⁵ to (2.9-11) for $\alpha = 0$ is $\gamma = A\sigma$, and the value of A is determined by

$$\frac{3h^3 Z}{16\pi^2 [r\sqrt{2mkT}]^3} = I_{\frac{1}{2}}(A). \quad (2.13)$$

For a perturbation, we let $\gamma = A\sigma + \epsilon(\sigma)$ where ϵ is supposed small when α is small. Equation (2.9) becomes,

$$\begin{aligned} \epsilon''(\sigma) &= \alpha^{\frac{2}{3}} \sigma I_{\frac{1}{2}} \left(A + \frac{\epsilon(\sigma)}{\sigma} \right) \\ &= \alpha^{\frac{2}{3}} \sigma I_{\frac{1}{2}}(A) + \frac{1}{2} \alpha^{\frac{2}{3}} I_{-\frac{1}{2}}(A) \epsilon(\sigma) + \dots, \end{aligned} \quad (2.14)$$

and (2.10) becomes

$$\epsilon(0) = \alpha^{\frac{2}{3}}. \quad (2.15)$$

Hence to leading order in α by (2.14-15) we get the terms,

$$\epsilon(\sigma) = \alpha^{\frac{2}{3}} + B\sigma + 0 \cdot \sigma^2 + \frac{\alpha^{\frac{2}{3}} \sigma^3}{6} I_{\frac{1}{2}}(A) + o(\alpha^{\frac{2}{3}}). \quad (2.16)$$

The term B drops out of (2.11) so we must impose the normalization directly by integration of the number density,

$$\rho = \frac{4\pi(2mkT)^{\frac{3}{2}}}{h^3} I_{\frac{1}{2}} \left(A + \frac{\epsilon(\sigma)}{\sigma} \right), \quad (2.17)$$

over the sphere. Thus expanding $I_{\frac{1}{2}}$ in ϵ we get,

$$\begin{aligned} Z &= 16\pi^2 c^3 \alpha \left(\frac{2mkT}{h^2} \right)^{\frac{3}{2}} \int_0^{\sigma_b} \left[I_{\frac{1}{2}}(A) + \frac{1}{2} \left(\frac{\alpha^{\frac{2}{3}}}{\sigma} \right. \right. \\ &\quad \left. \left. + B + \frac{\alpha^{\frac{2}{3}} \sigma^2}{6} I_{\frac{1}{2}}(A) \right) I_{-\frac{1}{2}}(A) \right] \sigma^2 d\sigma, \end{aligned} \quad (2.18)$$

where σ_b is given from r_b by (2.8). Now A is determined by (2.13) such that the first term on the right-hand-side exactly cancels the Z , so the rest of (2.18) must vanish by itself. Thus, doing the integrals of σ^n we can solve for B and it is,

$$B = -3 \left[\frac{\alpha^{\frac{2}{3}}}{2\sigma_b} + \frac{\alpha^{\frac{2}{3}} I_{\frac{1}{2}}(A) \sigma_b^2}{30} \right]. \quad (2.19)$$

According to Feynman *et al.*³, the equation for the pressure, P , in terms of surface quantities is,

$$\begin{aligned} \frac{P\Omega}{N} &= \frac{2}{9} Z kT \left(\frac{r_b^3}{c^3 \alpha} \right) I_{\frac{3}{2}} \left(A + \frac{\alpha^{\frac{2}{3}}}{\sigma_b} + B \right. \\ &\quad \left. + \frac{\alpha^{\frac{2}{3}} \sigma_b^2}{6} I_{\frac{1}{2}}(A) \right) = \frac{2}{9} Z kT \left(\frac{r_b^3}{c^3 \alpha} \right) \left[I_{\frac{3}{2}}(A) \right. \\ &\quad \left. + \frac{3}{2} I_{\frac{1}{2}}(A) \left\{ -\frac{\alpha^{\frac{2}{3}}}{2\sigma_b} + \frac{2\alpha^{\frac{2}{3}} \sigma_b^2}{30} I_{\frac{1}{2}}(A) \right\} \right], \end{aligned} \quad (2.20)$$

to leading order. This expression reduces to

$$\begin{aligned} \frac{P\Omega}{N} &= \frac{2}{9} Z kT \left(\frac{r_b^3}{c^3 \alpha} \right) I_{\frac{3}{2}}(A) \\ &\quad \times \left[1 - \frac{9 I_{\frac{1}{2}}(A)}{20 I_{\frac{3}{2}}(A)} \left(\frac{Z e^2}{r_b kT} \right) + \dots \right], \end{aligned} \quad (2.21)$$

where the first term gives the ideal Fermi gas pressure and the second term gives the first correction to it.

In order to compute the next order, we must consider the remainder after subtraction of the above result. The key part is the behavior of $I_{\frac{1}{2}}(A + (\epsilon/\sigma)) - I_{\frac{1}{2}}(A) - \frac{1}{2} I_{-\frac{1}{2}}(A) \epsilon/\sigma$ in the normalization integral which determines B of (2.16). The reason that this part might not be expanded in a straightforward manner is that as $\sigma \rightarrow 0$, $\epsilon/\sigma \rightarrow \infty$. This effect could be important when we reach this order. The nonexpandable part of the contribution to the integral in (2.18) beyond the ideal Fermi gas contribution becomes,

$$\begin{aligned} &\int_0^{\sigma_b} \left[I_{\frac{1}{2}}(\hat{A} + \alpha^{\frac{2}{3}}/\sigma) - I_{\frac{1}{2}}(\hat{A}) \right] \sigma^2 d\sigma \\ &= \int_0^{\sigma_b} \sigma^2 d\sigma \int_0^{\infty} y^{\frac{1}{2}} dy \left[\frac{1}{\exp(y - \hat{A} - \alpha^{\frac{2}{3}}/\sigma) + 1} \right. \\ &\quad \left. - \frac{1}{\exp(y - \hat{A}) + 1} \right], \end{aligned} \quad (2.22)$$

where $\hat{A} = A + (\epsilon(\sigma) - \alpha^{\frac{2}{3}})/\sigma$. Let us set $y = \eta + \alpha^{\frac{2}{3}}/\sigma$ in the first term in the y integrand and $y = \eta$ in the second. Then (2.22) becomes,

$$\begin{aligned} &= \int_0^{\sigma_b} \sigma^2 d\sigma \left[\int_{-\alpha^{\frac{2}{3}}/\sigma}^0 \frac{d\eta (\eta + \alpha^{\frac{2}{3}}/\sigma)^{\frac{1}{2}}}{\exp(\eta - \hat{A}) + 1} \right. \\ &\quad \left. + \int_0^{\infty} \frac{d\eta [(\eta + \alpha^{\frac{2}{3}}/\sigma)^{\frac{1}{2}} - \eta^{\frac{1}{2}}]}{\exp(\eta - \hat{A}) + 1} \right]. \end{aligned} \quad (2.23)$$

The second integral in the large square brackets is directly expandable in $\alpha^{\frac{2}{3}}$ and gives the first order correction to the ideal Fermi gas which we have calculated above. Thus if we explicitly make this separation and if we let $\xi = -\eta/\alpha^{\frac{2}{3}}$ and reversing the order of integration in the first integral, (2.23) reduces to,

$$\begin{aligned} &= \frac{1}{2} \alpha^{\frac{2}{3}} \int_0^{\sigma_b} \sigma d\sigma I_{-\frac{1}{2}}(\hat{A}) \\ &\quad + \alpha \int_0^{\infty} d\xi \int_0^{\min(\sigma_b, 1/\xi)} \frac{(\sigma - \xi \sigma^2)^{\frac{1}{2}} \sigma d\sigma}{\exp(-\alpha^{\frac{2}{3}} \xi - \hat{A}) + 1} \\ &\quad + \int_0^{\sigma_b} \sigma^2 d\sigma \int_0^{\infty} \frac{d\eta [(\eta + \alpha^{\frac{2}{3}}/\sigma)^{\frac{1}{2}} - \eta^{\frac{1}{2}} - \frac{1}{2} \alpha^{\frac{2}{3}}/(\eta^{\frac{1}{2}} \sigma)]}{\exp(\eta - \hat{A}) + 1}, \end{aligned} \quad (2.24)$$

where as we remarked above the first term is the usual direct expansion term. The second and third terms (proportional to α) are the Debye-Huckel order correction that we seek. We begin by concentrating on the second term. Since, if we first do the integral over σ it makes the integral over ξ convergent without reference to the exponential in the denominator, we can set $\alpha = 0$ directly in the exponential, to leading order. If we make the change of variables, $s = \sigma\xi$ and $t = \xi\sigma_b$ then the part of (2.24) proportional to α becomes

$$\frac{\alpha\sigma_b^{\frac{3}{2}}\gamma_{DH}}{1+e^{-A}}, \quad \gamma_{DH} = \int_0^\infty \frac{dt}{t^{\frac{5}{2}}} \int_0^{\min(t,1)} (s-s^2)^{\frac{1}{2}} s ds. \quad (2.25)$$

The quantity γ_{DH} is now just a number. We may rewrite it as,

$$\begin{aligned} \gamma_{DH} &= \int_0^1 \frac{d\eta}{\eta^{\frac{5}{2}}} \int_0^\eta (s-s^2)^{\frac{1}{2}} s ds \\ &\quad + \left(\int_1^\infty \frac{d\eta}{\eta^{5/2}} \right) \left(\int_0^1 s^{\frac{3}{2}} (1-s)^{\frac{1}{2}} ds \right) \\ &= \int_0^1 \frac{d\eta}{\eta^{\frac{5}{2}}} \int_0^\eta (s-s^2)^{\frac{1}{2}} s ds + \frac{\pi}{24}, \end{aligned} \quad (2.26)$$

as the second integral now factors into the product of a beta function integral and a simple power integral. Now if we let $s = \eta\tau$ in the first integral and integrate first over η and then over τ , which again involves a beta function integral, we get

$$\gamma_{DH} = \frac{4}{9} - \frac{\pi}{24} + \frac{\pi}{24} = \frac{4}{9}. \quad (2.27)$$

Next we will do the third term in (2.24). If we do the integral over σ first and make the change of variables $x = \eta\sigma_b/\alpha^{\frac{2}{3}}$, then we get, as we did going from (2.24) to (2.25),

$$\begin{aligned} &\frac{\alpha\sigma_b^{\frac{3}{2}}}{3(1+e^{-A})} \int_0^\infty \left[(1+x)^{\frac{3}{2}} - \frac{3(1+2x)(1+x)^{\frac{1}{2}}}{8x} - \frac{3}{4}x^{\frac{1}{2}} \right. \\ &\quad \left. - x^{\frac{3}{2}} + \frac{3}{16x^{\frac{3}{2}}} \log(1+2(x+x^2)^{\frac{1}{2}}+2x) \right] \frac{dx}{x}. \end{aligned} \quad (2.28)$$

We have choosen to evalutate this integral numerically. To ease the labor it is convenient to add and subtract the identity,

$$\begin{aligned} &-\frac{3}{32} \int_0^\infty \log(1+8x^2) \frac{dx}{x^{\frac{5}{2}}} + \frac{3}{2} \int_0^\infty \frac{dx}{x^{\frac{1}{2}}(1+x)} \\ &\quad \equiv (-2^{-\frac{5}{4}} + 1.5)\pi. \end{aligned} \quad (2.29)$$

The result for the third term of (2.24) (at least to 6 figures) is

$$-\frac{4}{9} \frac{\alpha\sigma_b^{\frac{3}{2}}}{1+e^{-A}}, \quad (2.30)$$

which exactly cancels the results of the second term! This cancellation could have been seen by the direct expansion of (2.22) plus an argument bounding the order in α of the large ϵ/σ effects on (2.22) to show that the next order term is of order $\alpha^{\frac{4}{3}}$. Since we are studying the structure, and in more realistic cases we do not expect that the Debye-Huckel order correction will vanish, we will continue to carry this term in subsequent calculations, but with a zero coefficient.

To obtain the $\alpha^{\frac{4}{3}}$ order term we return to (2.14) which we have now seen to be adequate to this task. If we substitute a power series in σ and solve for the coefficients, we get

$$\begin{aligned} \epsilon(\sigma) &= \alpha^{\frac{2}{3}} + B\sigma + \frac{1}{4}\alpha^{\frac{4}{3}}I_{-\frac{1}{2}}(A)\sigma^2 \\ &\quad + \left(\frac{1}{6}\alpha^{\frac{2}{3}}I_{\frac{1}{2}}(A) + \frac{1}{12}\alpha^{\frac{2}{3}}I_{-\frac{1}{2}}(A)B \right) \sigma^3 \\ &\quad + \frac{1}{240}\alpha^{\frac{4}{3}}I_{-\frac{1}{2}}(A)I_{\frac{1}{2}}(A)\sigma^5 + o(\alpha^{\frac{4}{3}}), \end{aligned} \quad (2.31)$$

which improves the result in (2.16).

If we now gather up these results and put them back as the next terms in (2.18), we find B through order $\alpha^{\frac{4}{3}}$ to be,

$$\begin{aligned} B &= -3 \left[\frac{\alpha^{\frac{2}{3}}}{2\sigma_b} + \frac{\alpha^{\frac{2}{3}}I_{\frac{1}{2}}(A)\sigma_b^2}{30} + \frac{\alpha^{\frac{4}{3}}I_{-\frac{1}{2}}(A)\sigma_b}{16} \right. \\ &\quad \left. + \frac{\alpha^{\frac{4}{3}}I_{-\frac{1}{2}}(A)I_{\frac{1}{2}}(A)\sigma_b^4}{1680} \right] \left(1 + \frac{\alpha^{\frac{2}{3}}I_{-\frac{1}{2}}(A)\sigma_b^2}{20} \right)^{-1} \\ &\quad - \frac{8\alpha \cdot 0}{3\sigma_b^{\frac{3}{2}}I_{-\frac{1}{2}}(A)(1+e^{-A})}. \end{aligned} \quad (2.32)$$

It is useful at this point to introduce a variable which measures the relative strength of the Coulomb interaction,

$$y = \left(\frac{Ze^2}{r_b kT} \right)^{\frac{1}{2}} = \left(\frac{\alpha c}{r_b} \right)^{\frac{1}{2}}. \quad (2.33)$$

In terms of y we find easily that $\alpha/\sigma_b^{\frac{3}{2}} = y^3$. Hence, substituting for B in (2.31), we obtain,

$$\epsilon(\sigma_b)/\sigma_b = -\frac{3}{10}y^2 + \frac{97}{2800} \frac{I_{-\frac{1}{2}}(A)}{I_{\frac{1}{2}}(A)} y^4 + o(y^4). \quad (2.34)$$

Using these results in the equation for the pressure, analogously to (2.20), we extend the expansion to give,

$$\begin{aligned} \frac{P\Omega}{ZNkT} &= \frac{2I_{\frac{3}{2}}(A)}{3I_{\frac{1}{2}}(A)} - \frac{3}{10}y^2 - \frac{0 \cdot 8y^3}{I_{-\frac{1}{2}}(A)(1+e^{-A})} \\ &\quad + \frac{97I_{-\frac{1}{2}}(A)y^4}{2800I_{\frac{1}{2}}(A)} + \dots, \end{aligned} \quad (2.35)$$

III. THERMODYNAMIC FUNCTIONS NEAR THE HOT CURVE

In addition to the pressure, which we discussed in the previous section, there are a few more quantities of interest in practical applications. Particularly there is the Helmholtz free energy \mathcal{A} , the internal energy U , and the number of ionized electrons, Z_i per atom. This latter quantity is a little hard to define with precision. The definition which we adopt here is a common one. Namely, the density of electrons at the surface of the atom is multiplied by the volume of the atom and this quantity is taken as the number of ionized electrons. This quantity is needed for all values of density and temperature and not just near the hot curve, but turns out to be a function of only a single variable and so for convenience we discuss it here. This number is conveniently computed as the Z in equation (2.13), except that A in that equation is now the boundary value of γ/σ defined by (2.8). We may deduce this value from the pressure by means of (2.20). We may rewrite that equation as,

$$\frac{P\Omega}{N} = \frac{2}{9}ZkT \left(\frac{r_b^3}{c^3\alpha} \right) I_{\frac{3}{2}} \left(\frac{\gamma_b}{\sigma_b} \right). \quad (3.1)$$

It is desirable to introduce a convenient variable analogous to that for the ideal Fermi gas, which by (2.13) can be expressed as,

$$\zeta_i = \frac{Z_i N \lambda^3}{2\Omega} = \frac{2}{\sqrt{\pi}} I_{\frac{1}{2}}(\gamma_b/\sigma_b), \quad (3.2)$$

where

$$\lambda = \left(\frac{h^2}{2\pi m k T} \right)^{\frac{1}{2}}. \quad (3.3)$$

Using these variables, we can rewrite (3.1) as

$$\frac{P\Omega}{Z_i N k T} = \frac{2I_{\frac{3}{2}}(\gamma_b/\sigma_b)}{3I_{\frac{1}{2}}(\gamma_b/\sigma_b)} = g(\zeta_i), \quad (3.4)$$

or

$$\frac{P}{2kT} \left(\frac{h^2}{2\pi m k T} \right)^{\frac{3}{2}} = \zeta_i g(\zeta_i) \equiv f(\zeta_i). \quad (3.5)$$

The idea is to find γ_b/σ_b and substitute it into (3.2) and so compute the number of ionized electrons per atom. This can most conveniently be done, if we revert (3.5) and back substitute for ζ_i in (3.2), thus giving,

$$Z_i = \frac{8\pi r_b^3}{3} \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} f^{-1} \left(\frac{P}{2kT} \left[\frac{h^2}{2\pi m k T} \right]^{\frac{3}{2}} \right). \quad (3.6)$$

We have now obtained a formula to compute directly from the pressure, density and temperature, a thermodynamic expression for the number of free electrons per atom, independently of where the pressure formula came from. (The inclusion of exchange interactions in the uniform electron gas would modify the result.) The physics behind this result is that it produces that density of

uniform-Fermi-gas electrons which are in pressure equilibrium with our finite-radius, spherical Thomas-Fermi atoms at the given temperature. We remark that the limiting behavior is such that as $T \rightarrow 0$ the resulting expression is a formula for Z_i in terms of P and ρ with finite coefficients, as it should be.

Next we consider the Helmholtz free energy, \mathcal{A} . Thermodynamic theory tells us that

$$\left. \frac{\partial \mathcal{A}}{\partial \Omega} \right|_T = -P, \quad \left. \frac{\partial \mathcal{A}}{\partial T} \right|_\Omega = -S, \quad U = \mathcal{A} + TS, \quad (3.7)$$

where S is the entropy. We may integrate the first relation in (3.7) to obtain \mathcal{A} from P as

$$\mathcal{A} = \int_\Omega^{\hat{\Omega}} P(\Omega, T) \Omega \frac{d\Omega}{\Omega} + \mathcal{A}_{\hat{\Omega}}(T), \quad (3.8)$$

The function $\mathcal{A}_{\hat{\Omega}}(T)$ is determined by noting that the system is equivalent to an infinitely dilute Fermi gas in the infinite volume limit and taking $\hat{\Omega}$ large enough. In order to carry out this integration, let us rewrite, (2.35) in terms of the variables y of (2.33) and the de Broglie density,

$$\zeta \equiv \frac{ZN\lambda^3}{2\Omega} \equiv \frac{6\alpha c^3}{\sqrt{\pi} r_b^3} \equiv \frac{2}{\sqrt{\pi}} I_{\frac{1}{2}}(A(\zeta)), \quad (3.9)$$

which we now consider as the definition of ζ and $A(\zeta)$ with λ defined by (3.3). We get

$$\frac{P\Omega}{ZNkT} = g_0(\zeta) + g_1(\zeta)y + g_2(\zeta)y^2 + g_3(\zeta)y^3 + g_4(\zeta)y^4 + \dots, \quad (3.10)$$

where by (2.35), [note the comparison with (3.4) above],

$$\begin{aligned} g_0(\zeta) &= \frac{2I_{\frac{3}{2}}(A(\zeta))}{3I_{\frac{1}{2}}(A(\zeta))}, \\ g_1(\zeta) &= 0, \\ g_2(\zeta) &= -\frac{3}{10}, \\ g_3(\zeta) &= -\frac{8 \cdot 0}{3\sqrt{\pi}} \left[\frac{2I_{\frac{1}{2}}(A(\zeta))}{\zeta I_{-\frac{1}{2}}(A(\zeta)) [1 + \exp(-A(\zeta))]} \right] \\ &\equiv -\frac{8 \cdot 0}{3\sqrt{\pi}} \left[\frac{Y(\zeta)}{\zeta} \right], \\ g_4(\zeta) &= \frac{97I_{-\frac{1}{2}}(A(\zeta))}{2800I_{\frac{1}{2}}(A(\zeta))}, \\ &\dots \end{aligned} \quad (3.11)$$

Noting that $\zeta = 6y^6/(\sqrt{\pi}\alpha^2)$ and that $d\Omega/\Omega = -d\zeta/\zeta$ we may integrate (2.35) to give,

$$\begin{aligned} \mathcal{A}(\Omega, T) - \mathcal{A}_{\hat{\Omega}}(T) &= ZNkT \sum_{j=0}^4 \left\{ \frac{1}{\zeta^{\frac{j}{6}}} \int_0^\zeta g_j(\tau) \tau^{\frac{j}{6}-1} d\tau \right\} y^j + \dots \end{aligned} \quad (3.12)$$

Now Baker and Johnson⁵ give the result for the ideal Fermi gas,

$$\mathcal{A}_{\text{ideal}} = ZNkT \left[\log \zeta - 1 + \int_0^\zeta [g_0(\tau) - 1] \frac{d\tau}{\tau} \right], \quad (3.13)$$

and so we get for the Helmholtz free energy,

$$\begin{aligned} \mathcal{A}(\Omega, P) = ZNkT & \left[\log \zeta - 1 + \int_0^\zeta [g_0(z) - 1] \frac{dz}{z} \right. \\ & \left. + \sum_{j=1}^4 \left\{ \frac{1}{\zeta^{\frac{j}{6}}} \int_0^\zeta g_j(\tau) \tau^{\frac{j}{6}-1} d\tau \right\} y^j + \dots \right]. \end{aligned} \quad (3.14)$$

Finally in this section we give the results for the internal energy, U . From the last two relations in (3.7), we can compute from (3.14) that it is,

$$\begin{aligned} U(\Omega, T) = \mathcal{A} - T \frac{\partial \mathcal{A}}{\partial T} \Big|_\Omega &= \frac{3}{2} P\Omega \\ &- \frac{1}{4} ZNkT \left[\sum_{j=1}^4 \left\{ \frac{j}{\zeta^{\frac{j}{6}}} \int_0^\zeta g_j(\tau) \tau^{\frac{j}{6}-1} d\tau \right\} y^j + \dots \right]. \end{aligned} \quad (3.15)$$

IV. EVALUATION OF THE COEFFICIENTS OF THE PERTURBATION EXPANSION OFF THE HOT CURVE

A number of functions of the de Broglie density, ζ (3.9) [and ζ_i (3.2)] were defined in the previous section. We need convenient methods to assign numerical values to them. The basic information which we will use was derived by Baker and Johnson⁵ who from the known series for the ideal Fermi gas properties in powers of

$$z = e^A, \quad (4.1)$$

$$f^{-1}(x) \approx x \left[\frac{1 + 1.3611484x + 0.58267802x^2 + 0.082982138x^3 + 0.0024019352x^4}{1 + 1.8030901x + 1.1564449x^2 + 0.31377482x^3 + 0.032693781x^4 + 0.00080776954x^5} \right]^{\frac{2}{5}}. \quad (4.4)$$

The next quantity that we need a representation for is the Debye-Huckel order correction for the Thomas-Fermi model at general de Broglie density. The relevant function is $Y(\zeta)$ as defined by (3.11). Again the aforementioned series allow us to construct the necessary Taylor series to use Padé methods to derive an accurate representation. We may rewrite $Y(\zeta)$ directly in terms of the quantities for which the series are given as,

$$Y(\zeta) = (g(\zeta) + \zeta g'(\zeta)) \frac{z(\zeta)}{1 + z(\zeta)}, \quad (4.5)$$

where this expression was derived by the use of (2.12), (2.13), (4.1) and the thermodynamic consistency formula of Baker and Johnson,⁵

$$g(\zeta) + \zeta g'(\zeta) = \zeta \frac{d \log z(\zeta)}{d\zeta}. \quad (4.6)$$

with A defined by (2.13), derived the series expansions in ζ through the 36th order for $z(\zeta)$ and for $P\Omega/ZNkT$. In addition they developed a representation, good to about 0.1 per cent uniformly in ζ for the second of these quantities. As a reminder to the reader, it is,

$$\begin{aligned} g(\zeta) \approx & \quad (4.2) \\ & \left[\frac{1 + 0.61094880\zeta + 0.12660436\zeta^2 + 0.0091177644\zeta^3}{1 + 0.080618739\zeta} \right]^{\frac{1}{3}}, \end{aligned}$$

where $g(\zeta)$ is as given in (3.4) and is also $g_0(\zeta)$ of (3.10-11).

The next quantity that we need is for the number of ionized electrons and is $f^{-1}(x)$ defined by (3.5-6). Using the aforementioned series expansions, we can revert the series, and by the method of Padé approximants,⁶ deduce representations. As this method converges quickly for our case we can determine the accuracy of low order representations by comparison with the higher order ones. We have chosen to build in exactly the asymptotic value as $x \rightarrow \infty$

$$f^{-1}(x) \asymp \left[\frac{5}{2} \left(\frac{4}{3\sqrt{\pi}} \right)^{\frac{2}{3}} x \right]^{\frac{3}{5}}. \quad (4.3)$$

This asymptotic value, and subsequent ones, are derived from the known asymptotic value of $I_{\frac{1}{2}}(A)$ and relation (2.12). We find that, to within about 0.2 per cent uniformly in x ,

We again build in the asymptotic results,

$$Y(\zeta) \asymp \frac{2}{3} \left(\frac{3\sqrt{\pi}}{4} \right)^{\frac{2}{3}} \zeta^{\frac{2}{3}}. \quad (4.7)$$

We find, accurate to about 0.1 percent uniformly in ζ , that,

$$\begin{aligned} Y(\zeta) = & \quad (4.8) \\ & \zeta \left[\frac{1 + 0.19232340\zeta + 0.020189866\zeta^2}{1 + 1.0710031\zeta + 0.36793047\zeta^2 + 0.038559806\zeta^3} \right]^{\frac{1}{3}}. \end{aligned}$$

The coefficient for the term of order y^4 given by (3.11) can be written as a function of ζ by means of (2.12) and (4.6) as

$$\frac{2880}{97} g_4(\zeta) = \frac{1}{g(\zeta) + \zeta g'(\zeta)}. \quad (4.9)$$

Again the right hand side can be shown to be asymptotic to

$$\frac{3}{2} \left(\frac{4}{3\sqrt{\pi}} \right)^{\frac{2}{3}} \zeta^{-\frac{2}{3}}. \quad (4.10)$$

We find, accurate to about 0.1 percent uniformly in ζ , that,

$$g(\zeta) + \zeta g'(\zeta) \approx \left[\frac{u_5(\zeta)}{v_3(\zeta)} \right]^{\frac{1}{3}}, \quad (4.11)$$

where

$$\begin{aligned} u_5(\zeta) = & 1 + 1.2361522\zeta + 0.54327035\zeta^2 \\ & + 9.7985998 \times 10^{-2}\zeta^3 + 6.1912639 \times 10^{-3}\zeta^4 \\ & + 1.6191557 \times 10^{-4}\zeta^5, \end{aligned} \quad (4.12)$$

and

$$\begin{aligned} v_3(\zeta) = & 1 + 0.17549205\zeta + 1.1833437 \times 10^{-2}\zeta^2 \\ & + 3.0923597 \times 10^{-4}\zeta^3. \end{aligned} \quad (4.13)$$

In order to compute the Helmholtz free energy and the internal energy, we need the integrals in (3.14). That for g_1 is of course 0. That for g_2 is elementary, but we include it for completeness,

$$\frac{1}{\zeta^{\frac{1}{3}}} \int_0^\zeta g_2(\tau) \tau^{-\frac{2}{3}} d\tau = -\frac{9}{10}. \quad (4.14)$$

The integral for g_3 can be re-expressed by the use of form (4.5) and an integration by parts as,

$$\frac{1}{\zeta^{\frac{1}{2}}} \int_0^\zeta g_3(\tau) \tau^{-\frac{1}{2}} d\tau = -\frac{8 \cdot 0}{3\sqrt{\pi}} Z(\zeta), \quad (4.15)$$

where,

$$Z(\zeta) = \frac{\log(1+z(\zeta))}{\zeta} + \frac{1}{2\zeta^{\frac{1}{2}}} \int_0^\zeta \log(1+z(\tau)) \frac{d\tau}{\tau^{\frac{3}{2}}}. \quad (4.16)$$

Again using the aforementioned series, and the asymptote,

$$Z(\zeta) \asymp 4 \left(\frac{3\sqrt{\pi}}{4} \right)^{\frac{2}{3}} \zeta^{-\frac{1}{3}}, \quad (4.17)$$

we derive the representation, accurate to about 0.1 percent uniformly in ζ ,

$$Z(\zeta) \approx \left[\frac{p_6(\zeta)}{q_7(\zeta)} \right]^{\frac{1}{3}}, \quad (4.18)$$

where,

$$\begin{aligned} p_6(\zeta) = & 8 + 8.9135838\zeta + 3.7226651\zeta^2 + 0.71393824\zeta^3 \\ & + 6.0876790 \times 10^{-2}\zeta^4 + 1.7586257 \times 10^{-3}\zeta^5 \\ & + 4.0529048 \times 10^{-6}\zeta^6, \end{aligned} \quad (4.19)$$

and

$$\begin{aligned} q_7(\zeta) = & 1 + 1.4070911\zeta + 0.78167135\zeta^2 + 0.21585403\zeta^3 \\ & + 3.0398456 \times 10^{-2}\zeta^4 + 1.9605712 \times 10^{-3}\zeta^5 \\ & + 3.9279799 \times 10^{-5}\zeta^6 + 3.5835548 \times 10^{-8}\zeta^7. \end{aligned} \quad (4.20)$$

We will defer the derivation of the representation of the y^4 term to another time, since it will turn out that we are unlikely to need it.

Special to the Helmholtz free energy, but not required for the internal energy is the integral of (3.13). The asymptote is,

$$\int_0^\zeta [g(\tau) - 1] \frac{d\tau}{\tau} \asymp \frac{3}{5} \left(\frac{3\sqrt{\pi}}{4} \right)^{\frac{2}{3}} \zeta^{\frac{2}{3}}. \quad (4.21)$$

We can again derive by the method of Padé approximants the following representation, accurate to within about 0.1 percent uniformly in ζ

$$\int_0^\zeta [g(\tau) - 1] \frac{d\tau}{\tau} \approx \zeta \left[\frac{r_6(\zeta)}{s_7(\zeta)} \right]^{\frac{1}{3}}, \quad (4.22)$$

where

$$\begin{aligned} r_6(\zeta) = & 5.5242716 \times 10^{-3} + 8.3296356 \times 10^{-4}\zeta \\ & + 5.5685767 \times 10^{-5}\zeta^2 + 1.9354761 \times 10^{-6}\zeta^3 \\ & + 3.4637431 \times 10^{-8}\zeta^4 + 2.4471328 \times 10^{-10}\zeta^5 \\ & + 2.8694904 \times 10^{-13}\zeta^6, \end{aligned} \quad (4.23)$$

and

$$\begin{aligned} s_7(\zeta) = & 1 + 0.17878444\zeta + 0.014195594\zeta^2 \\ & + 6.1616726 \times 10^{-4}\zeta^3 + 1.5056878 \times 10^{-5}\zeta^4 \\ & + 1.8932201 \times 10^{-7}\zeta^5 + 9.2069935 \times 10^{-10}\zeta^6 \\ & + 7.5175901 \times 10^{-13}\zeta^7. \end{aligned} \quad (4.24)$$

V. EVALUATION OF THE THOMAS-FERMI THEORY COLD CURVE

The other limit for which information is known is the so-called cold curve. This region has been much more extensively studied than the hot curve. It is well known that the Thomas-Fermi cold curve leads to excessively high pressures in the region of normal material densities. It is not our purpose to provide a “good” representation of this cold curve, but only an adequate one to facilitate the main point of this article which is to study the structure of the Thomas-Fermi equation of state. To derive the equation for the cold curve from our starting point in Sec. II, (2.6-11), we need the change of variables,

$$x = \alpha^{\frac{1}{3}} \left(\frac{2}{3} \right)^{\frac{2}{3}} r/c = r/\mu, \quad \phi = \frac{r}{c\alpha} \left[\frac{eV(r)}{kT} - \eta \right]. \quad (5.1)$$

Then (2.9) becomes,

$$\frac{d^2\phi}{dx^2} = \frac{9x}{4\alpha^2} I_{\frac{1}{2}} \left(\frac{\phi(x)}{x} \alpha^{\frac{4}{3}} \left(\frac{2}{3} \right)^{\frac{2}{3}} \right) \rightarrow x \left(\frac{\phi(x)}{x} \right)^{\frac{3}{2}}, \quad (5.2)$$

as $\alpha \rightarrow \infty$. With this change of variables, the boundary conditions (2.10-11) can be expressed as

$$\phi(0) = 1, \quad \text{and} \quad (5.3)$$

$$\frac{d\phi}{dx} = \frac{\phi}{x}, \quad \text{at the boundary.} \quad (5.4)$$

It is easy to verify that

$$\phi(x) = \frac{144}{x^3}, \quad (5.5)$$

is a solution of (5.2) when $\alpha = \infty$, however it does not obey the boundary conditions. Sommerfeld⁷ has given the asymptotic behavior of the solution of (5.2) for large x in the case of the atom where (5.3) holds and (5.4) is replaced by $\lim_{x \rightarrow \infty} \phi(x) = 0$. His result is,

$$\phi(x) \asymp \left(1 + \left(\frac{x}{\sqrt[3]{144}} \right)^{-a_-} \right)^{-a_+/2}, \quad (5.6)$$

where

$$a_{\pm} = \frac{7 \pm \sqrt{73}}{2} \approx \begin{matrix} 7.77200187, \\ -0.77200187. \end{matrix} \quad (5.7)$$

For the case of all the electrons in a large but finite sphere, we need to impose the boundary condition (5.4). Suppose that $\phi_A(x)$ is the atomic solution. It is convenient to use

$$\phi(x) = \eta(x) \phi_A(x), \quad (5.8)$$

which converts (5.2) for $\alpha = 0$ to

$$\frac{d^2\eta}{dx^2} + \frac{2\phi'_A}{\phi_A} \frac{d\eta}{dx} = \left(\frac{\phi_A}{x} \right)^{\frac{1}{2}} \left(\eta^{\frac{3}{2}} - \eta \right) \quad (5.9)$$

If we make the further transformation, $\xi = \log x$, then we get

$$\frac{d^2\eta}{d\xi^2} - \left(1 + \frac{2\phi'_A}{\phi_A} x \right) \frac{d\eta}{d\xi} = (x^3 \phi_A)^{\frac{1}{2}} \left(\eta^{\frac{3}{2}} - \eta \right). \quad (5.10)$$

When x is large, (5.10) reduces to an equation which is independent of the independent variable,

$$\frac{d^2\eta}{d\xi^2} - 7 \frac{d\eta}{d\xi} + 12\eta = 12\eta^{\frac{3}{2}}. \quad (5.11)$$

The picture now is that when x_b [the radius of the sphere r_b as transformed by (5.1)] is large, then we have over most of the range of x the result that the solution η corresponds to that for the atom. However, η must increase

some as we near x_b to get in all Z electrons and compensate for the small number of electrons that lie beyond x_b in the atomic solution. As (5.11) is independent of the origin, we might as well normalize $\xi = \log(x/x_b)$ so the boundary is taken for the origin. As we are treating the asymptotic case $x_b \rightarrow \infty$, we derive in this picture the boundary conditions,

$$\eta(-\infty) = 1, \quad \frac{d\eta}{d\xi} = 4\eta \text{ at } \xi = 0. \quad (5.12)$$

If we now make the further transformation on (5.11), $p(\eta) = \eta'$, then we obtain a first-order, nonlinear ordinary differential equation,

$$pp' - 7p + 12(\eta - \eta^{\frac{3}{2}}) = 0. \quad (5.13)$$

Using these boundary conditions, we have solved (5.13) numerically using a four-point Runge-Kutta method with 256 steps to run from $\eta = 1$ to

$$\eta = \eta_0 \equiv \eta(0) = p(\eta)/4. \quad (5.14)$$

We find that

$$\eta_0 \approx 1.9958, \quad (5.15)$$

which is a universal constant that connects the asymptotic behavior of the atomic and the pressurized solutions in the form $\phi(x_b) \asymp \eta_0 \phi_A(x_b)$. We will apply this to (5.6) to yield,

$$\phi(x_b) \asymp \eta_0 \left(1 + \left(\frac{x_b}{\sqrt[3]{144}} \right)^{-a_-} \right)^{-a_+/2}, \quad (5.16)$$

which should be good for large enough values of x_b . Rather than attempting to derive an accurate, analytic representation of the Thomas-Fermi cold curve function, which is highly unrealistic in any event, we have found if we use the cold curve generated by the Liberman Thomas-Fermi-Dirac Los Alamos equation of state production code⁸ run in Thomas-Fermi mode, that the Thomas-Fermi cold-curve ϕ can be fit to within a few percent. To do so we note that we should have $\phi(x_b) \propto 1/x_b$ as $x_b \rightarrow 0$ and if we use the Sommerfeld variable to correct (5.16), we are lead to

$$\begin{aligned} \phi(x_b) \approx \eta_0 & \left(1 + ax_b^{a_-} + bx_b^{2a_-} \right)^{-1/(2a_-)} \\ & \times \left(1 + \left(\frac{x_b}{\sqrt[3]{144}} \right)^{-a_-} \right)^{-a_+/2}, \end{aligned} \quad (5.17)$$

where the fit yields $a = 1.59233$ and $b = 1.06595$. This corresponds to 100% of full ideal Fermi gas pressure for infinite density ($x_b \rightarrow 0$), which we expect as the kinetic energy dominates the Coulomb energy at infinite density. In terms of $\phi_b \equiv \phi(x_b)$ the cold-curve pressure is,

$$P = \frac{Z^2 e^2}{10\pi\mu^4} \left[\frac{\phi_b}{x_b} \right]^{\frac{5}{2}}. \quad (5.18)$$

In addition to the cold curve, it is useful to know in what way it is approached in T . This information can be derived from the asymptotic expression, (Huang⁹)

$$I_{\frac{1}{2}}(\eta) = \frac{2}{3}\eta^{\frac{3}{2}} \left[1 + \frac{\pi^2}{8\eta^2} + \cdots \right] + O(e^{-\eta}), \quad (5.19)$$

and similar expressions for $I_{\frac{3}{2}}(\eta)$ derived from (5.19) by means of (2.12). Huang⁹ gives the change in the pressure as a function of ϕ_b . It is

$$P = \frac{Z^2 e^2}{10\pi\mu^4} \left(\frac{\phi_b}{x_b} \right)^{\frac{5}{2}} \left[1 + \left(\frac{3}{2} \right)^{\frac{4}{3}} \frac{5\pi^2 x_b^2}{12\phi^2 \alpha^{\frac{8}{3}}} + \cdots \right]. \quad (5.20)$$

We have checked this correction against the Liberman⁸ code for cases where the correction should be a few percent and find agreement with that predicted by the code within the accuracy of our cold-curve fit. This correction is proportional to T^2 .

VI. GLOBAL REPRESENTATION OF THE THOMAS-FERMI FLUID PRESSURE

In order to take advantage of the results that we have obtained in the previous sections, we again use the method of Padé approximants.⁶ The problem to be solved is that we have, for small y (2.33), an expansion of the pressure (3.10-11) in powers of y with the coefficients exactly known functions of ζ (3.9). In addition we know that in the limit as the temperature goes to 0, we must have a non-identically zero function of the density. Since both y and ζ go to infinity in this limit, it must necessarily be the case that the coefficients $g_j(\zeta)$ of (3.11) must have the property,

$$\lim_{\zeta \rightarrow \infty} g_j(\zeta) \zeta^{(j-2)/3} = \hat{g}_j < \infty, \quad (6.1)$$

in order that a series of finite terms in $r_b^{\frac{1}{2}}$ remain. It is straightforward to verify that the functions given in (3.11) do in fact have this property, as can be noted explicitly from the representations given in Sec. IV. In addition we know that the leading correction to the zero temperature limit is proportional to T^2 or $\alpha^{-\frac{8}{3}}$ with appropriate density dependent coefficients. In order to impose all these conditions, it is useful to rewrite, as we did at (3.11),

$$y = \left(\frac{\sqrt{\pi}\zeta}{6} \right)^{\frac{1}{6}} \alpha^{\frac{1}{3}}, \quad (6.2)$$

which allows us to convert our series (3.10) in y into one in $\alpha^{\frac{1}{3}}$, but without the nice properties that the coefficients are of order unity for small ζ . Now we form an [8/8] two-point Padé-approximant-like form, on which we impose the conditions that it match the series expansion terms (3.10) through order y^3 ,

$$\frac{P\Omega}{ZNkT} = \sum_{j=0}^3 h_j(\zeta) \alpha^{\frac{j}{3}}, \quad (6.3)$$

for α small, and

$$P = H_0(r_b) + H_1(r_b) \alpha^{-\frac{8}{3}}, \quad (6.4)$$

for α large, where the $H_i(r_b)$ are given by (5.20). Such a form can be given as,

$$P = \frac{ZNkTg_0(\zeta)}{\Omega} \times \left[\frac{1 - \frac{\omega}{1-\omega} \sum_{j=2}^3 \frac{g_j(\zeta)}{g_0(\zeta)} y^j + \frac{H_0(r_b)}{H_1(r_b)} (1-\omega) \alpha^{\frac{8}{3}}}{1 - \frac{1}{1-\omega} \sum_{j=2}^3 \frac{g_j(\zeta)}{g_0(\zeta)} y^j + \frac{H_0(r_b)(1-\omega)}{H_1(r_b)\omega} \alpha^{\frac{8}{3}}} \right], \quad (6.5)$$

where we have partially re-expressed it in terms of y for convenience, and,

$$\omega = \frac{H_0(r_b)\Omega}{ZNkTg_0(\zeta)}. \quad (6.6)$$

This particular form has the advantage, not only of satisfying the conditions (6.3-4), but also with the signs known to occur for the different coefficients it has both numerator and denominator each consisting of a sum of all positive terms. Form (6.5) is not a true Padé approximant because we have imposed only 13 conditions by means of (6.3-4), while 17 conditions are required to determine an [8/8] Padé approximant.

If in addition we include the y^4 term, then (6.5) is modified so that

$$\sum_{j=2}^3 \frac{g_j(\zeta)}{g_0(\zeta)} y^j \mapsto \sum_{j=2}^4 \left(\frac{g_j(\zeta)}{g_0(\zeta)} y^j \right) - \frac{y^4}{1-\omega} \left(\frac{g_2(\zeta)}{g_0(\zeta)} \right)^2. \quad (6.7)$$

We have also tried this form, but the correction does not, as a practical matter, justify the extra effort to obtain it. It appears to be beneficial only in those regions where (6.5) is already excellent. It is also helpful where (6.5) does a very poor job as discussed below, but not sufficiently beneficial. Therefore we confine our attention to the form (6.5).

Figures 1 and 2 illustrate how well our global representation (6.5) does in reproducing the Thomas-Fermi pressure results for aluminum. The reader is reminded that all the Thomas-Fermi quantities simply scale as a function of the nuclear charge³ so except for differently scaled ranges of temperature, density and pressure, the results are the same for all elements. Over a substantial, many-decade sized region we have 5 % or better accuracy. Globally there are two regions in which the accuracy deteriorates to 20 % or worse.

VII. GLOBAL REPRESENTATION OF THE ELECTRON FLUID PRESSURE

In this section we review the ingredients which went into the representation for the Thomas-Fermi fluid pressure in the previous section with an eye to replacing them

with accurate determinations of the analogous quantities for a fluid of electrons and ions. First of all the ideal gas pressure, which is the leading order in the small y expansion (3.10) remains unchanged. In addition the coefficient of y^1 also remains correctly given as zero. The coefficient of y^2 is artificial in the Thomas-Fermi model. The correct value here is known to be the electron-exchange correction. It is the leading order perturbation away from the ideal Fermi gas in powers of the electronic charge e . In fact this perturbation has been carried out by the method of finite-temperature Green's functions by Abrikosov, *et al.*¹⁰ and the result that they obtain is the same as that written down previously by Cowan and Ashkin.⁴ It is,

$$\frac{P_{\text{exch}}}{kT} = -\frac{16\pi e^2 m^2 kT}{3h^4} \int_0^\infty \int_0^\infty \frac{\log \left| \frac{\sqrt{y_1} + \sqrt{y_2}}{\sqrt{y_1} - \sqrt{y_2}} \right| dy_1 dy_2}{(e^{y_1 - \eta} + 1)(e^{y_2 - \eta} + 1)}, \quad (7.1)$$

where, as this result is a perturbation off the ideal Fermi gas of electrons, η will be the constant value $A(\zeta)$ determined by (2.13) and (3.9), independent of the radius r . To compute this exchange correction we need to evaluate the function,

$$X(\zeta) = \int_0^\infty \int_0^\infty \frac{\log \left| \frac{\sqrt{y_1} + \sqrt{y_2}}{\sqrt{y_1} - \sqrt{y_2}} \right| dy_1 dy_2}{(e^{y_1 - \eta} + 1)(e^{y_2 - \eta} + 1)}. \quad (7.2)$$

In order to do this evaluation, we first make the substitution, $y_i = t_i^2$, so we get,

$$X(\zeta) = 4 \int_0^\infty \int_0^\infty \frac{\log \left| \frac{t_1 + t_2}{t_1 - t_2} \right| t_1 t_2 dt_1 dt_2}{(e^{t_1^2 - \eta} + 1)(e^{t_2^2 - \eta} + 1)}, \quad (7.3)$$

and expand the denominators in a power series as,

$$X(\zeta) = \sum_{n_1, n_2=1}^\infty (-1)^{n_1+n_2} \int_0^\infty \int_0^\infty t_1 t_2 dt_1 dt_2 \times \exp((n_1 + n_2)\eta - n_1 t_1^2 - n_2 t_2^2) \log \left| \frac{t_1 + t_2}{t_1 - t_2} \right|. \quad (7.4)$$

If we now make the change to polar coordinates,

$$r \cos \phi = \sqrt{n_1} t_1, \quad r \sin \phi = \sqrt{n_2} t_2, \quad (7.5)$$

the integrals factor into the product of two one-dimensional integrals,

$$\begin{aligned} X(\zeta) &= 2 \sum_{n_1, n_2=1}^\infty \frac{(-z)^{n_1+n_2}}{n_1 n_2} \left(\int_0^\infty r^3 e^{-r^2} dr \right) \\ &\quad \times \int_0^{\frac{\pi}{2}} \sin 2\phi \log \left| \frac{1 + \sqrt{\frac{n_1}{n_2}} \tan \phi}{1 - \sqrt{\frac{n_1}{n_2}} \tan \phi} \right| d\phi, \\ &= \sum_{n_1, n_2=1}^\infty \frac{(-z)^{n_1+n_2}}{n_1 n_2} \\ &\quad \times \int_0^{\frac{\pi}{2}} \sin 2\phi \log \left| \frac{1 + \sqrt{\frac{n_1}{n_2}} \tan \phi}{1 - \sqrt{\frac{n_1}{n_2}} \tan \phi} \right| d\phi, \end{aligned} \quad (7.6)$$

where $z = e^\eta$ as at (4.1). Since the $n_1 n_2$ and $n_2 n_1$ always appear symmetrically, we may as well sum the symmetrical pairs first. When we do this operation the integrals in the sum become, after the use of some simple trigonometric identities,

$$\int_0^{\frac{\pi}{2}} \sin 2\phi \log \left| \frac{1 + \lambda \sin 2\phi}{1 - \lambda \sin 2\phi} \right| d\phi, \quad (7.7)$$

where

$$\lambda = \frac{1}{2} \left(\sqrt{\frac{n_1}{n_2}} + \sqrt{\frac{n_2}{n_1}} \right) \geq 1. \quad (7.8)$$

Now the integral (7.7) can be further re-expressed as

$$\frac{1}{4} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} (e^{i\theta} + e^{-i\theta}) \log \left| \frac{(1 + r e^{i\theta})(1 + r e^{-i\theta})}{(1 - r e^{i\theta})(1 - r e^{-i\theta})} \right| d\theta, \quad (7.9)$$

where

$$\lambda = \frac{2r}{1 + r^2}. \quad (7.10)$$

For the case $\lambda < 1$ which in turn implies that $r < 1$, (7.9) can be expanded in powers of r and using the observation that

$$\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} e^{2ni\pi} d\theta = 0, \quad n \neq 0, \quad (7.11)$$

one finds directly that the integral (7.9) is just πr . For the case which we seek, $\lambda \geq 1$, the same result is obtained, when the absolute value signs in (7.9) are removed. It turns out that for our case, the answer is just the real part always. That is,

$$\begin{aligned} \int_0^{\frac{\pi}{2}} \sin 2\phi \log \left| \frac{1 + \lambda \sin 2\phi}{1 - \lambda \sin 2\phi} \right| d\phi \\ = \begin{cases} \pi(1 - \sqrt{1 - \lambda^2})/\lambda, & \lambda < 1 \\ \pi/\lambda, & \lambda \geq 1 \end{cases} \end{aligned} \quad (7.12)$$

Thus, substituting into (7.6), we get,

$$X(\zeta) = \pi \sum_{n_1, n_2=1}^\infty \frac{(-z)^{n_1+n_2}}{\sqrt{n_1 n_2} (n_1 + n_2)}. \quad (7.13)$$

It is interesting to note that by (7.13),

$$\begin{aligned} z \frac{dX(\zeta)}{dz} &= \pi \sum_{n_1, n_2=1}^\infty \frac{(-z)^{n_1+n_2}}{\sqrt{n_1 n_2}} = \\ &= \pi \left(- \sum_{n=1}^\infty \frac{(-z)^n}{\sqrt{n}} \right)^2 \equiv \left(I_{-\frac{1}{2}}(\eta) \right)^2, \end{aligned} \quad (7.14)$$

where $I_n(\eta)$ is defined by (2.2). If we use the connection between z and ζ (3.9) and the relation (4.6), we can re-express X directly in terms of ζ as,

$$X(\zeta) = \int_0^\zeta \frac{\pi \tau d\tau}{g(\tau) + \tau g'(\tau)}. \quad (7.15)$$

From the asymptotic behavior of $g(\zeta)$ as $\zeta \rightarrow \infty$ we can derive,

$$X(\zeta) \asymp 2 \left(\frac{3\sqrt{\pi}}{4} \right)^{\frac{4}{3}} \zeta^{\frac{4}{3}}, \quad (7.16)$$

which allows the computation of $g_2(\zeta)$ via (7.1).

Following the results of Gell-Mann and Brueckner,¹¹ we believe it is quite possible to give the Debye-Huckel correction, $g_3(\zeta)$, exactly for general ζ , but have not yet done so. If this task were done, following the same methods as in Sec. IV, one could produce the necessary exact expansions about the hot-curve for the pressure, internal energy, Helmholtz free energy, *etc.* that we gave in Sec. IV for the Thomas-Fermi model.

Next we consider the ingredients used near $T = 0$. Specifically, these were the cold-curve, *i.e.*, the pressure as a function of the density, and the leading correction in temperature, given by (5.20). For a realistic case these quantities are hard to calculate from first principles, but one can measure them and fit the results to one's favorite model. We need the cold curve (electron pressure as a function of density at zero temperature) and the leading correction in temperature. This quantity may be estimated for example (when the electronic specific heat vanishes linearly with temperature) from the relation,

$$\left. \frac{\partial^2 P}{\partial T^2} \right|_V = \gamma \lim_{T \rightarrow 0} C_V/T, \quad (7.17)$$

where γ is the Grüneisen parameter. With these determinations of the H_i in (6.4), we are again in a position to compute the pressure representation (6.5), this time for realistic materials. It will have the correct limiting behavior near the hot curve and the observed behavior near the cold curve. In between we expect it to extrapolate in a reasonable manner. If the Thomas-Fermi theory is a good guide, this region is a, relatively speaking, fairly small (but rather important) one. In the low-temperature-low-density region, such effects as phase transitions, due to changes of state or ionization of a few electrons, atomic shell structure and so forth would at present have to be built in as a correction to the reference function on a individual substance basis as might be appropriate. These effects are, of course, also extremely important in the regions near normal density and low temperature. Reference functions for other thermodynamic functions such as internal energy and the Helmholtz free energy can be constructed, we believe, by the same methods.

Finally there remains the computation of the degree of ionization for problems which include the exchange correction. Again the definition is somewhat arbitrary. For example, the Thomas-Fermi-Dirac model at $T = 0$ leads⁴ to a finite, atomic-surface electron-density at zero pressure. Thus in the presence of the exchange correction the simple idea used in Sec. III to determine the number of ionized electrons will require adjustment. Plainly, as

the pressure drops to zero, the number of ionized electrons should also fall to zero proportionally.

The pressure, including just the ideal gas pressure and the exchange correction, is, by (3.4) and (7.1-2),

$$\frac{P\Omega}{NkT} = Z_i g(\zeta_i) - \frac{16\pi e^2 m^2 k T \Omega}{3N h^4} X(\zeta_i), \quad (7.18)$$

or following the method of (3.5),

$$\frac{P}{2kT} \left(\frac{h^2}{2\pi m k T} \right)^{\frac{3}{2}} = \zeta_i g(\zeta_i) - \frac{4e^2 m}{3h(2\pi m k T)^{\frac{1}{2}}} X(\zeta_i). \quad (7.19)$$

Now as long as T is large enough so that the coefficient of $X(\zeta_i)$ is not too large, since $g(0) = 1$, $X(0) = 0$, and since as $\zeta_i \rightarrow \infty$ $\zeta_i g(\zeta_i) \propto \zeta_i^{\frac{5}{3}}$, $X \propto \zeta_i^{\frac{4}{3}}$, the predicted pressure in (7.19) will stay positive. However if T is small enough, the electron gas pressure given by (7.19) can be negative. This strange situation arises from the artificial split of the electron-electron energy into an exchange energy and a potential energy. The electron-electron potential is in turn paired with the ion-electron potential energy for convenience in the usual central field approach, which is common to the Thomas-Fermi model and related approaches. The total pressure, so calculated, should, of course, be non-negative. We know that (7.19) is good near the hot curve in the sense that it is a correct perturbation expansion. If we use the Padé method,⁶ we are lead to,

$$\frac{P}{2kT} \left(\frac{h^2}{2\pi m k T} \right)^{\frac{3}{2}} = \frac{\zeta_i g(\zeta_i)}{1 + \frac{4e^2 m}{3h(2\pi m k T)^{\frac{1}{2}}} \frac{X(\zeta_i)}{\zeta_i g(\zeta_i)}} \equiv \hat{f}(\zeta_i, T). \quad (7.20)$$

This form retains the accuracy in the neighborhood of the hot curve where after all we expect there to be high ionization. As $T \rightarrow 0$ for fixed density, the exchange correction in the denominator is proportional to r_b so the form reduces to the ideal Fermi gas result in the high density limit, but has relatively stronger ionization in the dilute case for the same pressure. It has the physical property that we described above that $P = 0$ corresponds to $\zeta_i = 0$ and *vice versa*. Thus, following (3.6), we obtain the formula,

$$Z_i = \frac{8\pi r_b^3}{3} \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} \hat{f}^{-1} \left(\frac{P}{2kT} \left[\frac{h^2}{2\pi m k T} \right]^{\frac{3}{2}}, T \right), \quad (7.21)$$

where the inverse is with respect to the argument ζ_i with T held fixed. This result should provide good accuracy for Z_i in the strongly ionized regions and will take Z_i to zero when the pressure is much less than that for the ideal Fermi gas, as expected.

REFERENCES

1. L. H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1927). E. Fermi, Z. Physik **48**, 73 (1928).

2. P. A. M. Dirac, Proc. Cambridge Philos. Soc. **26**, 376 (1930).
3. R. P. Feynman, N. Metropolis and E. Teller, Phys. Rev. **73**, 1561 (1949).
4. R. D. Cowan and J. Ashkin, Phys. Rev. **105**, 144 (1957).
5. G. A. Baker, Jr. and J. D. Johnson, to be published, *Proceedings of the Thirteenth International Workshop on Condensed Matter Physics*, August 6-12, 1989, Campos do Jordão, São Paulo, Brazil, (Plenum Press, New York, 1990).
6. G. A. Baker, Jr. and P. R. Graves-Morris, *Padé Approximants, Part I: Basic Theory, and Part II: Applications and Extensions, Encyclopedia of Mathematics and its Applications*, Vol. 13 and 14, G.-C. Rota, ed., (Cambridge Univ. Press, London, 1981).
7. A. Sommerfeld, Z. Physik **78**, 283 (1932).
8. D. A. Liberman, private communication (1980). This computer code is a programming of the Thomas-Fermi theory of ref. 3.
9. K. Huang, *Statistical Mechanics* (John Wiley & Sons, New York, 1963).
10. A. A. Abrikosov, L. P. Gorkov and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics*, R. A. Silverman, trans. (Prentice-Hall, Englewood Cliffs, N.J., 1963).
11. M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**,

364 (1957).

Figure Captions

Fig. 1. Comparison of the Thomas-Fermi pressure with our global representation for aluminum. The solid lines are the isotherms for the Thomas-Fermi pressure, while the broken curves are our representation. Shown is the high density region in (a) and the low density region in (b) with temperatures ranging from zero to 1.16×10^9 degrees Kelvin. Away from zero temperature the isotherms are essentially equally spaced in the logarithm, with the lowest nonzero temperature being 5.8×10^3 degrees Kelvin. In (a) a number of isotherms are coincident with that for zero temperature.

Fig. 2. Rough contours of percentage errors. The contours for percentage differences between the exact Thomas-Fermi and our global representation (6.5) in the pressure for aluminum are shown from -20% through $+20\%$. The -1% and -10% contours are not labeled but can be inferred from their location relative to the other contours. On a plus contour, the Thomas-Fermi pressure is higher than that for our global representation.